# MkIV ground-based measurements of Ethene (Ethylene; $C_2H_4$)

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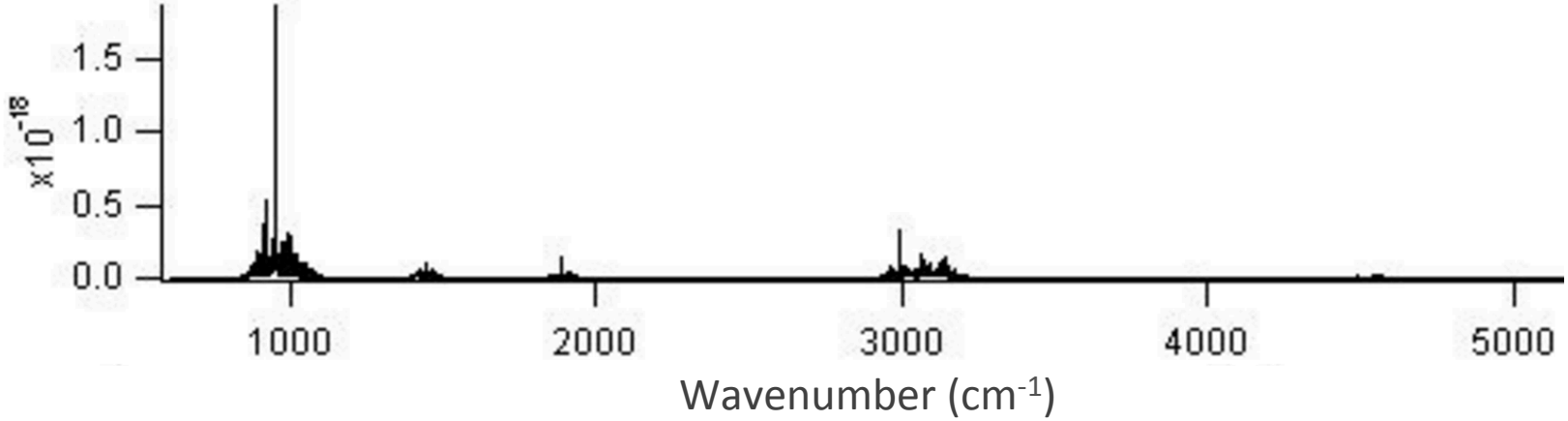
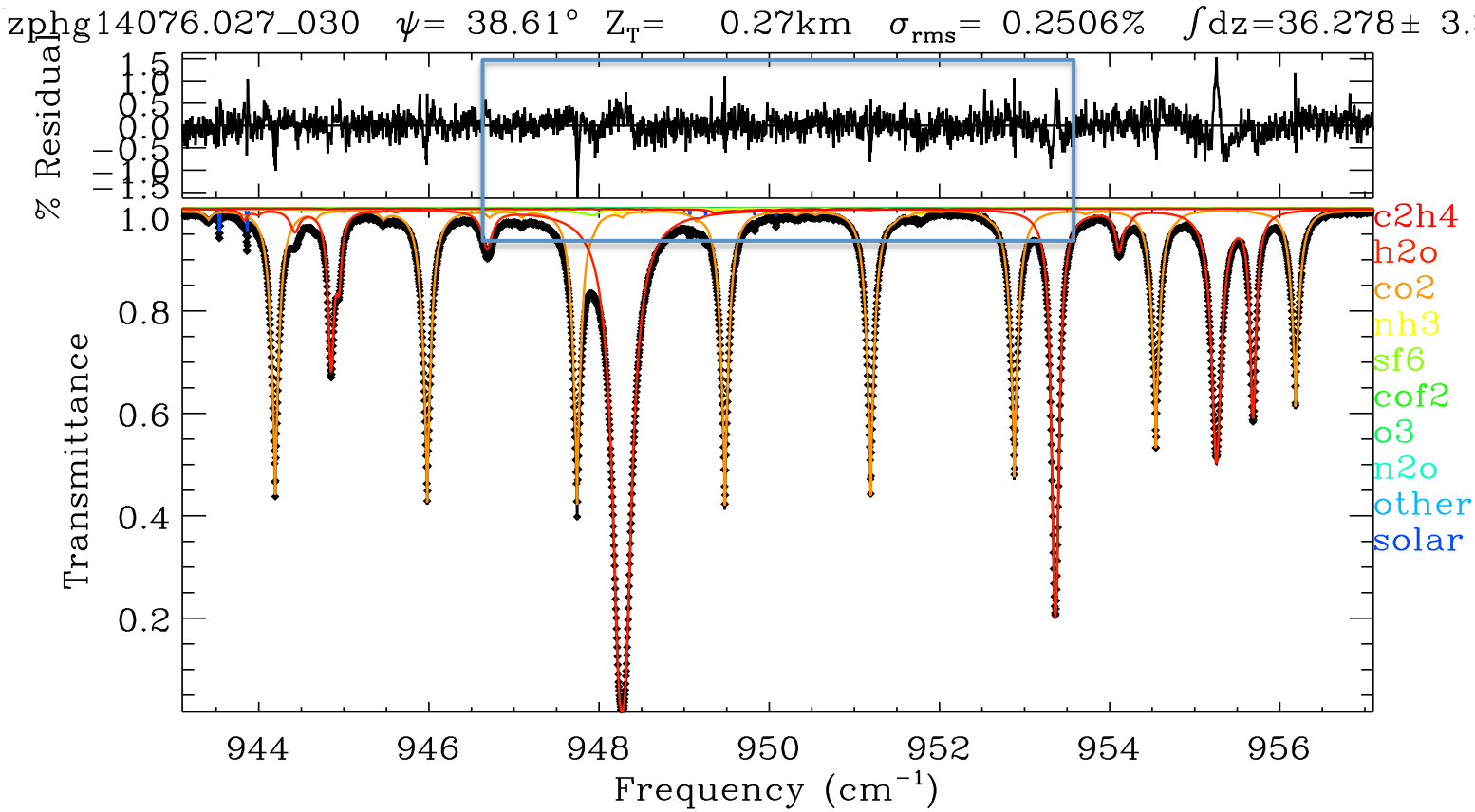
$C_2H_4$ has been previously measured by ACE (e.g., Herbin et al., 2009) and from the ground in fires (Paton-Walsh et al., 2005; Rinsland et al., 2005).

Best IR feature of $C_2H_4$ is Q-branch of $nu_7$ band ($CH_2$ wag) at 948 $cm^{-1}$. This is 7 times stronger than any feature in the 3000 $cm^{-1}$ region.

**Ethylene images from PNNL**



# Example of Fit to MkIV Spectrum from JPL



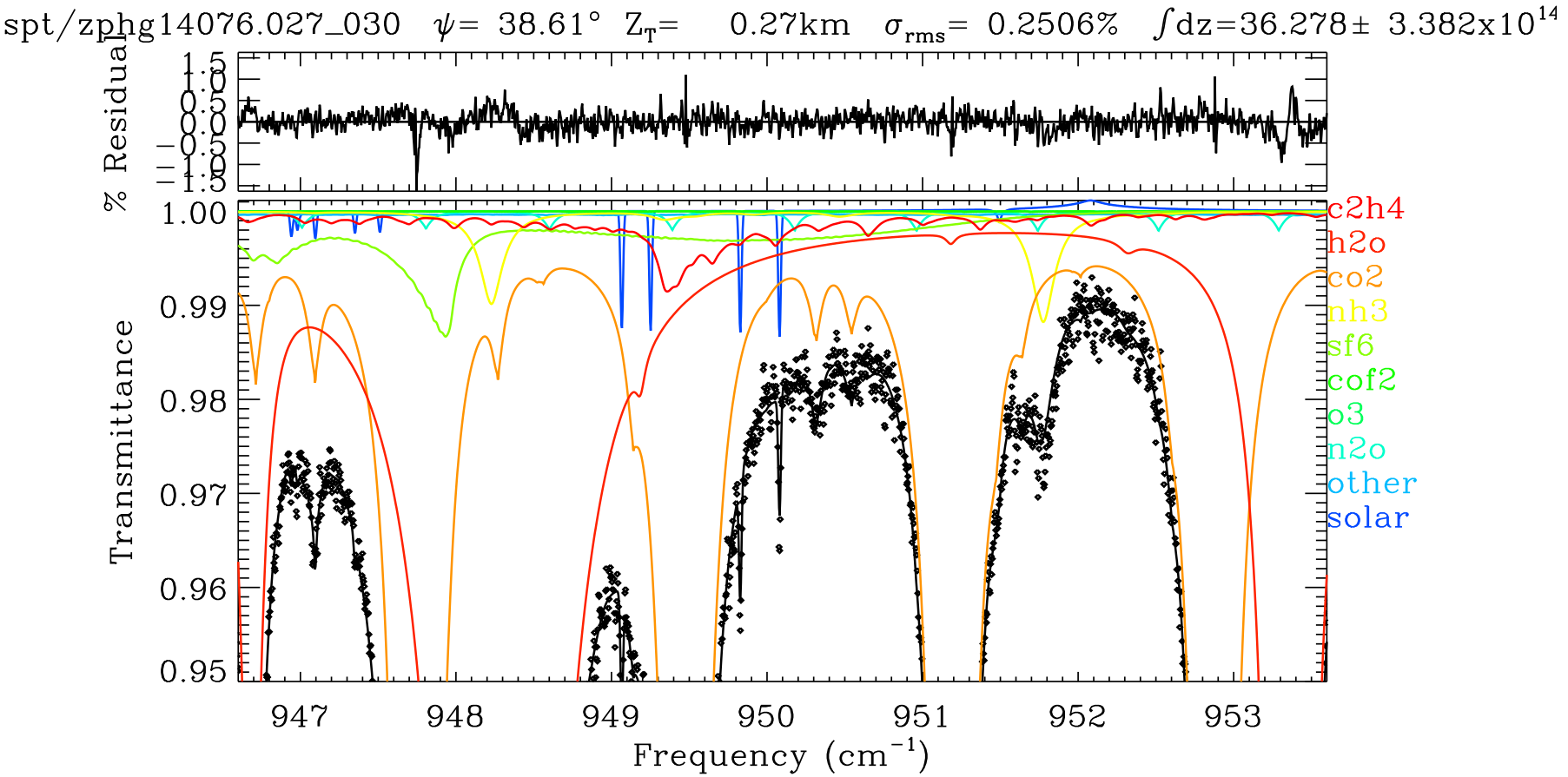

Defined a 14 $cm^{-1}$ wide window which include several strong lines of $CO_2$ and $H_2O$.

$CO_2$ lines are T-dependent, one lies directly overlies $C_2H_4$ Q-branch.

Fitting done using GFIT, NCEP model, ATM linelist (i.e., TCCON methodology).

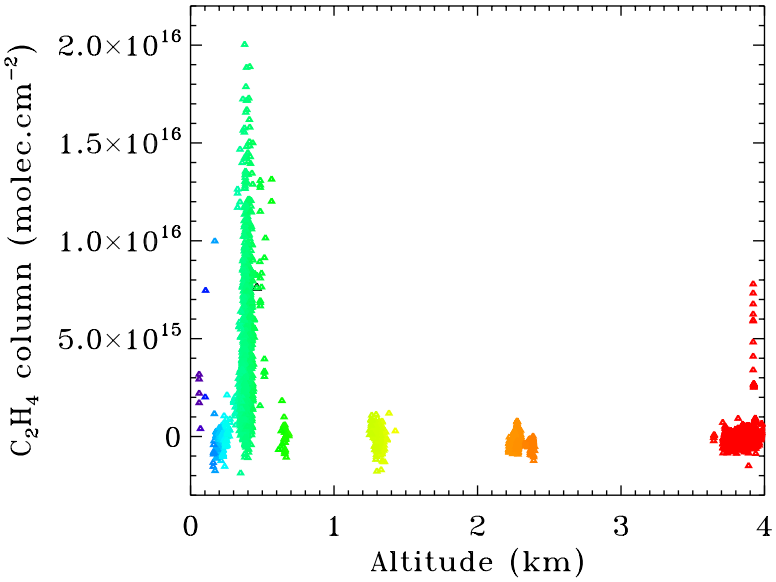
$C_2H_4$ Q-branch at 949.4 $cm^{-1}$ < 1% deep and therefore not discernable on this plot.

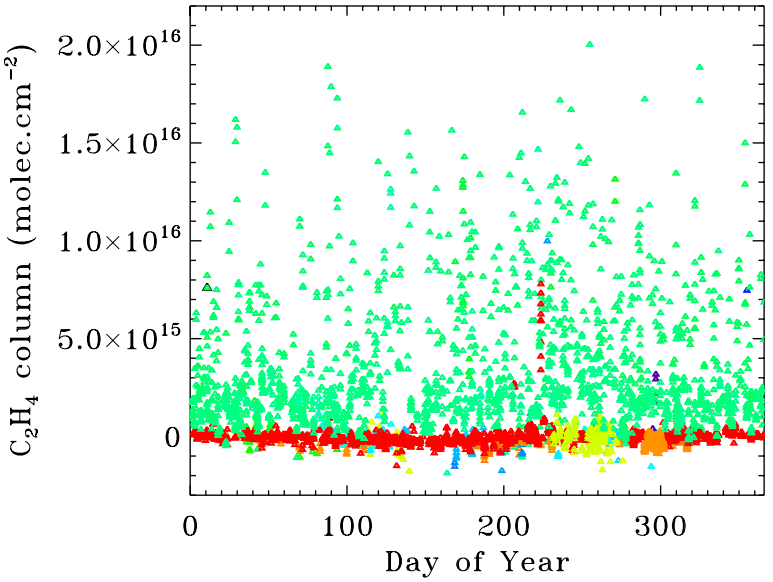
# Zoom into Spectral Fit

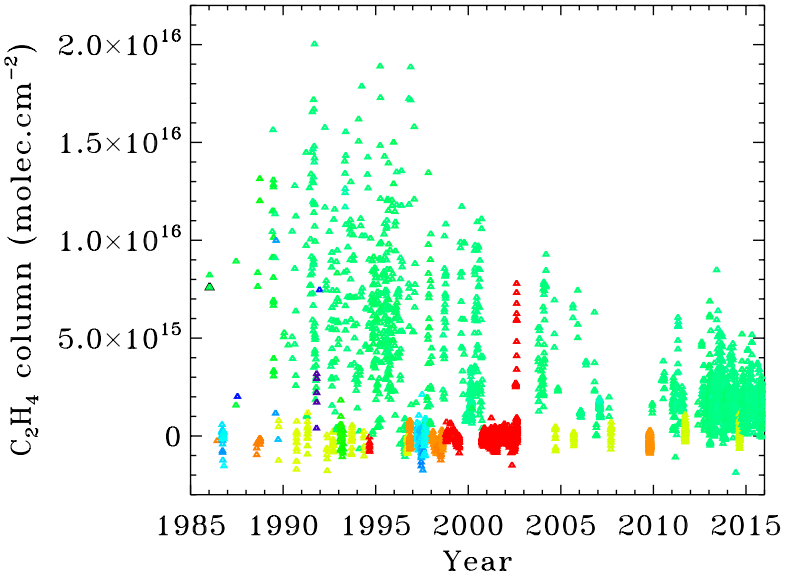



$C_2H_4$ Q-branch (red) peaks at 949.4 $cm^{-1}$. It is typically less than 1% deep even at JPL. It lies under a 60%-deep T-dependent $CO_2$ line centered at 949.5 $cm^{-1}$, the wing of a saturated $H_2O$ line centered at 948.3 $cm^{-1}$, and the $SF_6$ R-branch.

# Retrieved MkIV $C_2H_4$ columns from 12 sites




CO column (molec.cm$^{-2}$)

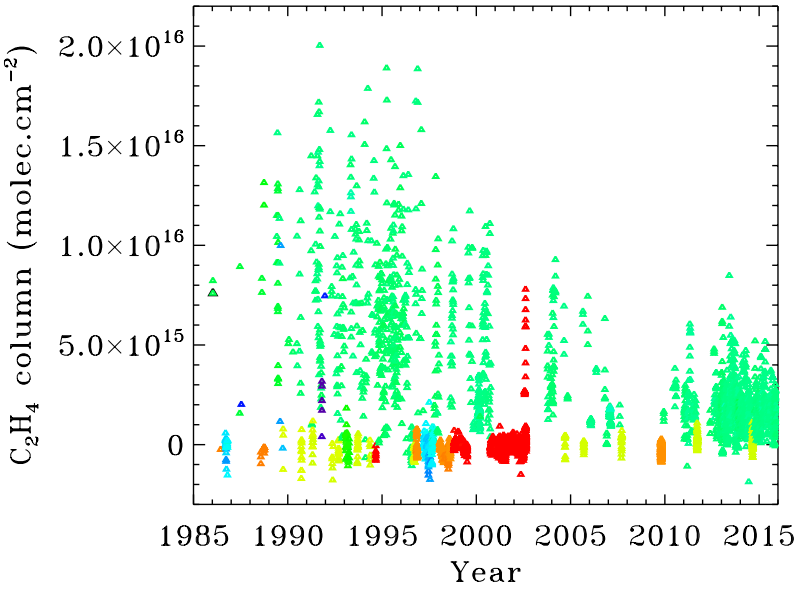
- Points color-coded by altitude.
- JPL (green) and Ames (purple) are only sites with non-zero $C_2H_4$
- Ft Sumner (lime), occasionally measures high $C_3H_8$, but always measures zero $C_2H_4$
- At JPL (green) $C_2H_6$ is highly variable without an obvious seasonal cycle.
- JPL $C_2H_4$ (green) has decreased by a factor 2-3 over the past 25 years

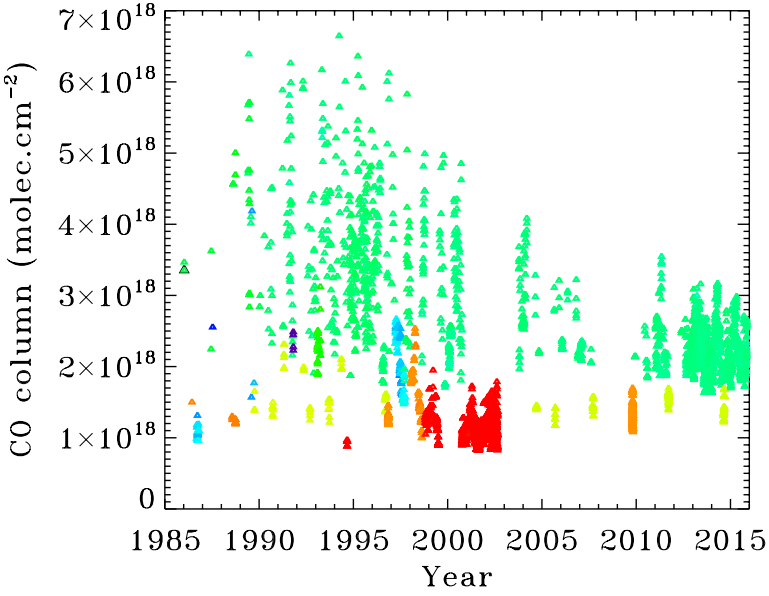
# MkIV $C_2H_4$ / CO correlation

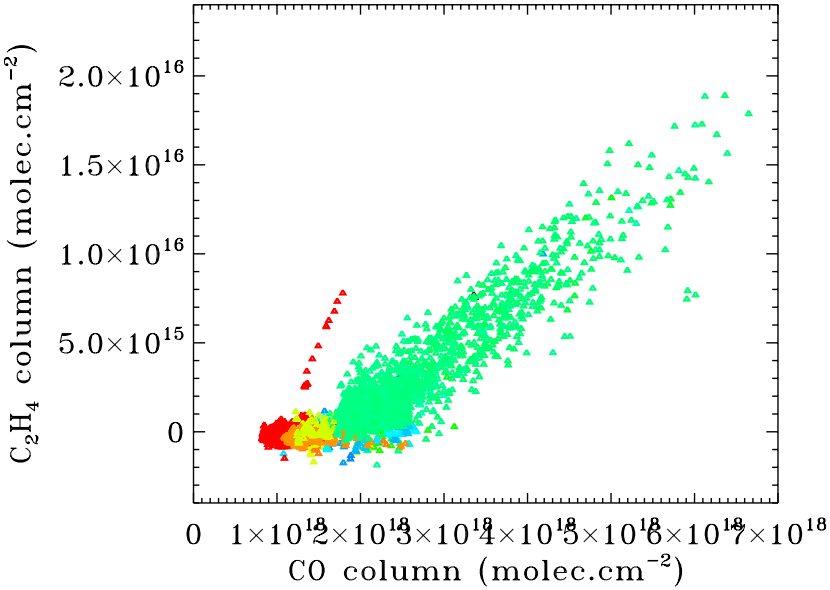
Plot color-coded by altitude, as in previous plot

CO also shows a large decrease over the past 25 years, such that the $C_2H_4$/CO correlation is very good at JPL.

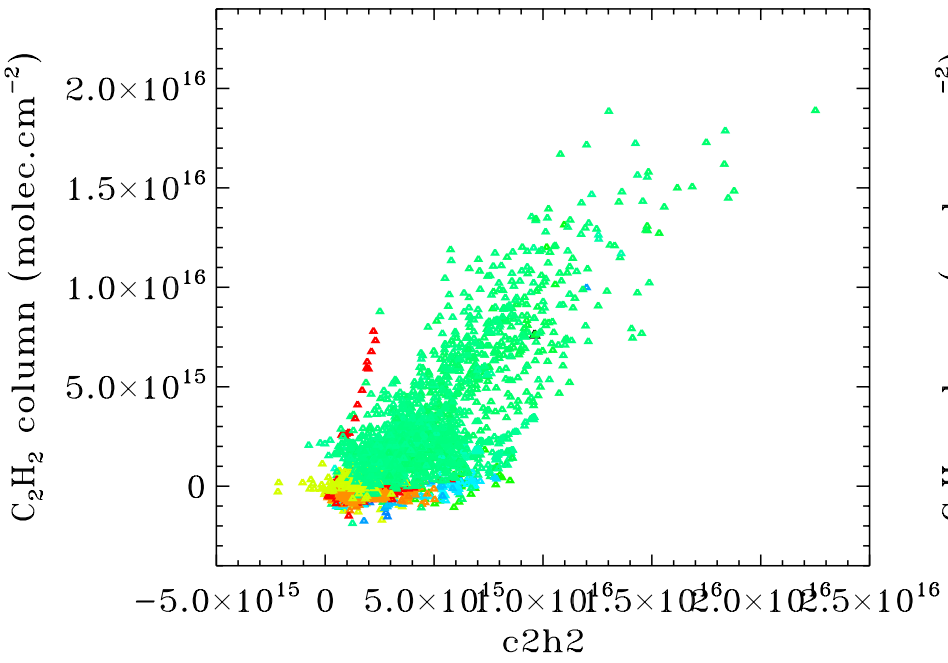
Implies common sources for $C_2H_4$ and CO, i.e. urban pollution.

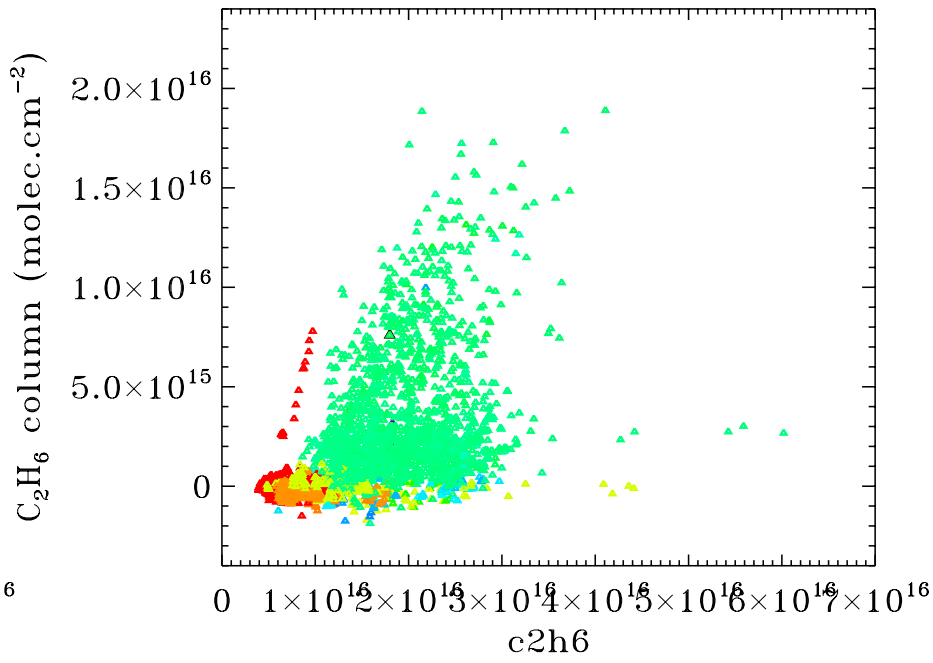


# $C_2H_4$ correlations with $C_2H_6$ and $C_2H_2$




$C_2H_4$ correlations with $C_2H_6$ and $C_2H_2$ are positive, but not as good as those with CO.

# Comparison with surface in-situ obs



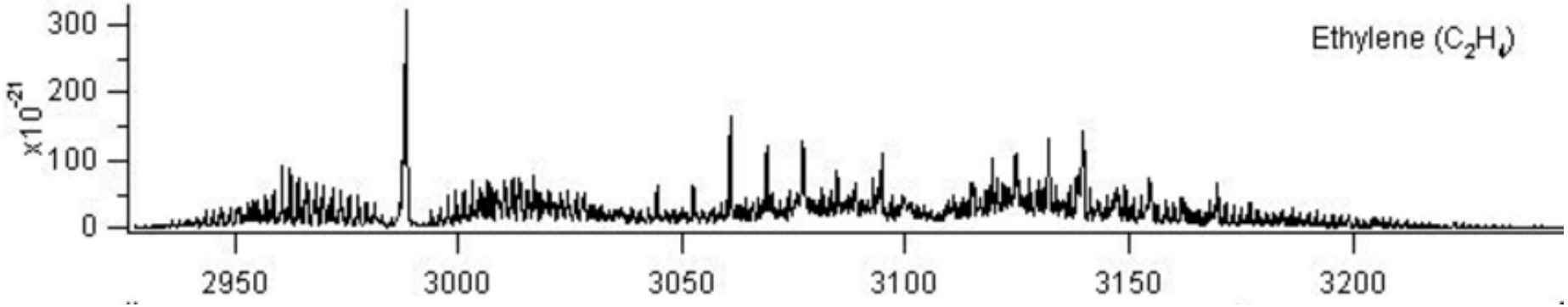
**Table 2.** Master Chemical Mechanism Model Results and Comparison to Measurements

| VOC | Initial Concentration (ppbv) | Residual BL Concentration[a] (ppbv) | Emission Ratio VOC/$C_2H_2$ | Measured Concentration[b] (ppbv) | Modeled Concentration[c] (ppbv) | Model-Measured Difference[d] (%) |
|---|---|---|---|---|---|---|
| Ethyne | 0.12[e] | 0.24 | 1.00[f] | 1.78 | 1.78 | 0 |
| Ethene | 0.065[e] | 0.065 | 1.36[f] | 2.16 | 1.88 | −13 |
| Benzene | 0.039[e] | 0.040 | 0.19[f] | 0.36 | 0.34 | −4 |
| Toluene | 0.017[e] | 0.028 | 0.82[f] | 0.83 | 1.19 | 44 |
| m,p-Xylene | 0[g] | 0 | 0.37[f] | 0.32 | 0.40 | 26 |
| o-Xylene | 0[g] | 0 | 0.14[f] | 0.14 | 0.17 | 21 |
| 1-Ethylbenzene | 0[g] | 0.003 | 0.10[f] | 0.14 | 0.14 | 2 |
| n-Propylbenzene | 0[g] | 0 | 0.028[f] | 0.022 | 0.040 | 82 |
| Isopropylbenzene | 0[g] | 0 | 0.009[f] | 0.007 | 0.013 | 86 |
| 1,2,3-Trimethylbenzene | 0[g] | 0 | 0.027[f] | 0.029 | 0.022 | −24 |
| 1,2,4-Trimethylbenzene | 0[g] | 0 | 0.12[f] | 0.089 | 0.10 | 16 |
| Isoprene | 0[g] | 0.003 | N/A | 1.09 | 1.09 | 0 |
| alpha-Pinene | 0[g] | 0 | N/A | 0.052 | 0.052 | 0 |
| Methyl vinyl ketone | 0.14[g] | 0.065 | $1.6 \times 10^{-3}$[h] | 0.48 | 0.41 | −14 |
| Methacrolein | 0.006[g] | 0.008 | $4.8 \times 10^{-3}$[h] | 0.18 | 0.24 | 37 |
| Glyoxal | 0 | 0 | $6.5 \times 10^{-5}$[h] | 0.19 | 0.18 | −5 |
| Acetaldehyde | 0.26[i] | 0.5[j] | 0.5[f] | 3.39 | 2.19 | −35 |

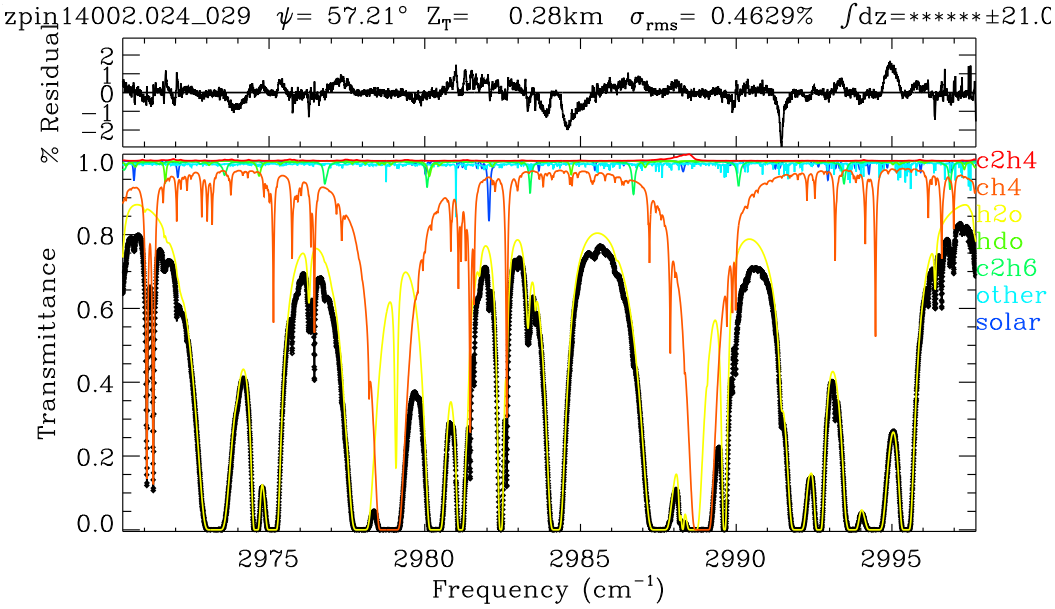
Ethene

Washenfelder [2011] measured 2.16 ppb of $C_2H_4$ (Ethene) at ground level in Pasadena, CA. Assuming that this was uniformly distributed throughout the PBL of 150 mbar thickness, the column would be $6 \times 10^{15}$ molecules/cm$^2$. MkIV $C_2H_4$ columns at JPL in the 2010 timeframe range from 0 to $6 \times 10^{15}$ and so are consistent.

# 3000 $cm^{-1}$ region – hopeless




Measuring $C_2H_4$ in the 3000 $cm^{-1}$ region will be difficult. The strongest feature, the $nu_{11}$ Q-branch at 2988.5 $cm^{-1}$, is 7 times weaker than the 949 $cm^{-1}$ feature. Even worse, it coincides with a saturated $H_2O$ line. Perhaps one or two of the Q-branches in the 3060 to 3140 $cm^{-1}$ region are usable, but these are 15 times weaker than the one at 949 $cm^{-1}$.



# $C_2H_4$ Summary/Conclusions

$C_2H_4$ can be measured from sea-level when columns exceed ~2E+15 molec./$cm^2$

I was skeptical at first that $C_2H_4$ could be retrieved, since its Q-branch is less than 1% deep and is hidden behind a 60% deep $CO_2$ line that is strongly T-dependent.

But the results are convincing: Under clear, unpolluted conditions $C_2H_4$ is always zero, whereas in big cities it is highly variable, correlating with CO.

The fact that the fitted window contains 7 other $CO_2$ lines of similar E" (on average) seems to lessen the impact of $CO_2$ and T uncertainties on the $C_2H_4$ retrievals.

$C_2H_4$ has a strong correlation with CO, implying similar sources (urban pollution). But $C_2H_4$'s lifetime is much shorter and so it quickly falls to zero away from sources.

When fitting $SF_6$ from polluted site, $C_2H_4$ must be included as an interferent.

No chance of retrieving $C_2H_4$ from the 3000 $cm^{-1}$ region, e.g., with a TCCON instrument equipped with an InSb detector.

# Aliso Canyon gas leak

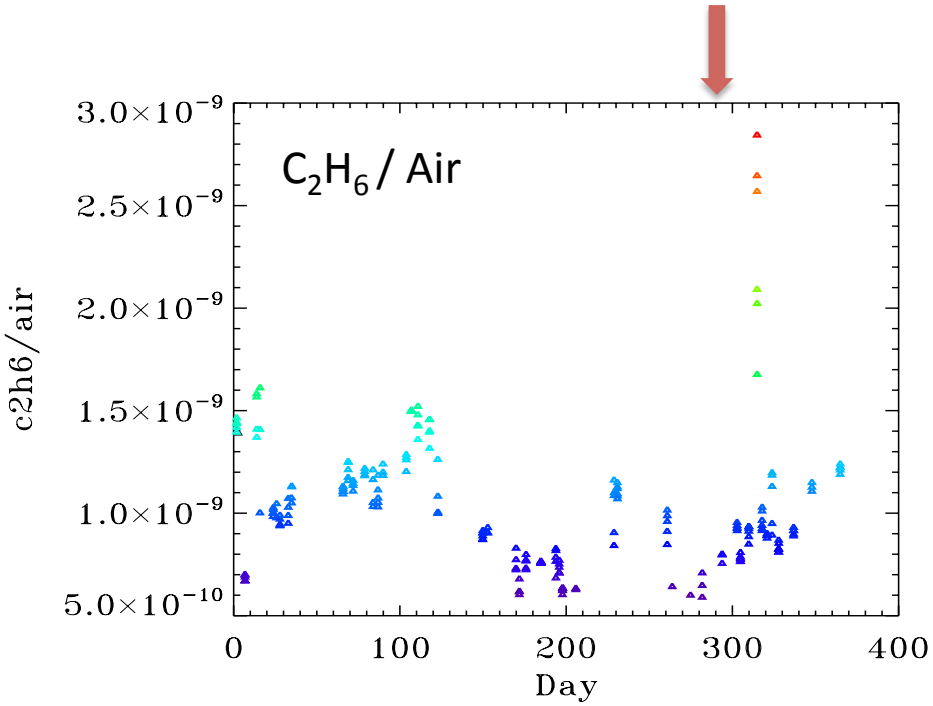
From Wikipedia, the free encyclopedia

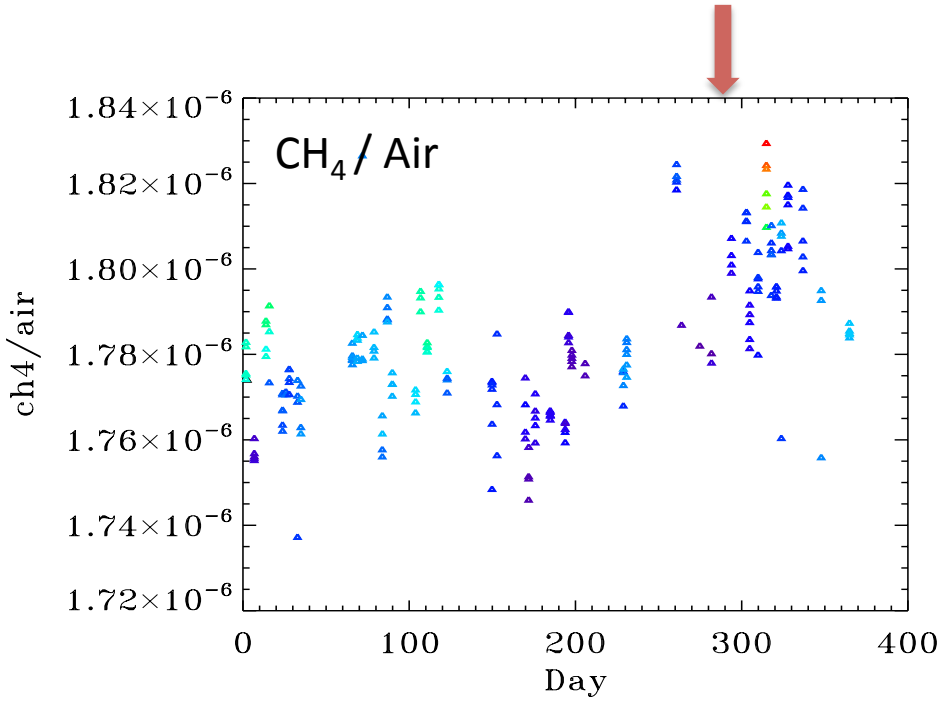
The **Aliso Canyon gas leak** (also called **Porter Ranch gas leak**[1] and **Porter Ranch gas blowout**[2]) was a massive natural gas leak that was discovered by SoCalGas employees on October 23, 2015.[3] Gas was released from a well within the Aliso Canyon's underground storage facility in the Santa Susana Mountains near Porter Ranch, Los Angeles.[4] The second-largest gas storage facility of its kind in the United States, it belongs to the Southern California Gas Company, a subsidiary of Sempra Energy. On January 6, 2016, Governor Jerry Brown issued a state of emergency.[5] The Aliso gas leak carbon footprint is said to be larger than the Deepwater Horizon leak in the Gulf of Mexico. On February 11, 2016 the gas company reported that it had the leak under control.[6]

On February 18, 2016, state officials announced that the leak was permanently plugged. An estimated 97,100 tonnes (95,600 long tons; 107,000 short tons) of methane and 7,300 tonnes (7,200 long tons; 8,000 short tons) of ethane was released into the atmosphere,[7] making it the worst natural gas leak in U.S. history in terms of its environmental impact.[8][9][10]

Aliso Canyon Underground Storage Facility is located 40 km from JPL. Jan 4 LA Times states that NG leak began Oct 23, 2015 and peaked on Nov 28 at 60 Tons of $CH_4$ per hour. By Dec 22 leak rate had decreased to 30 Tons per hour as the underground storage pressure dropped from the initial 2700 psi.

# MkIV 2015 $C_2H_6$ and $CH_4$ Time Series from JPL



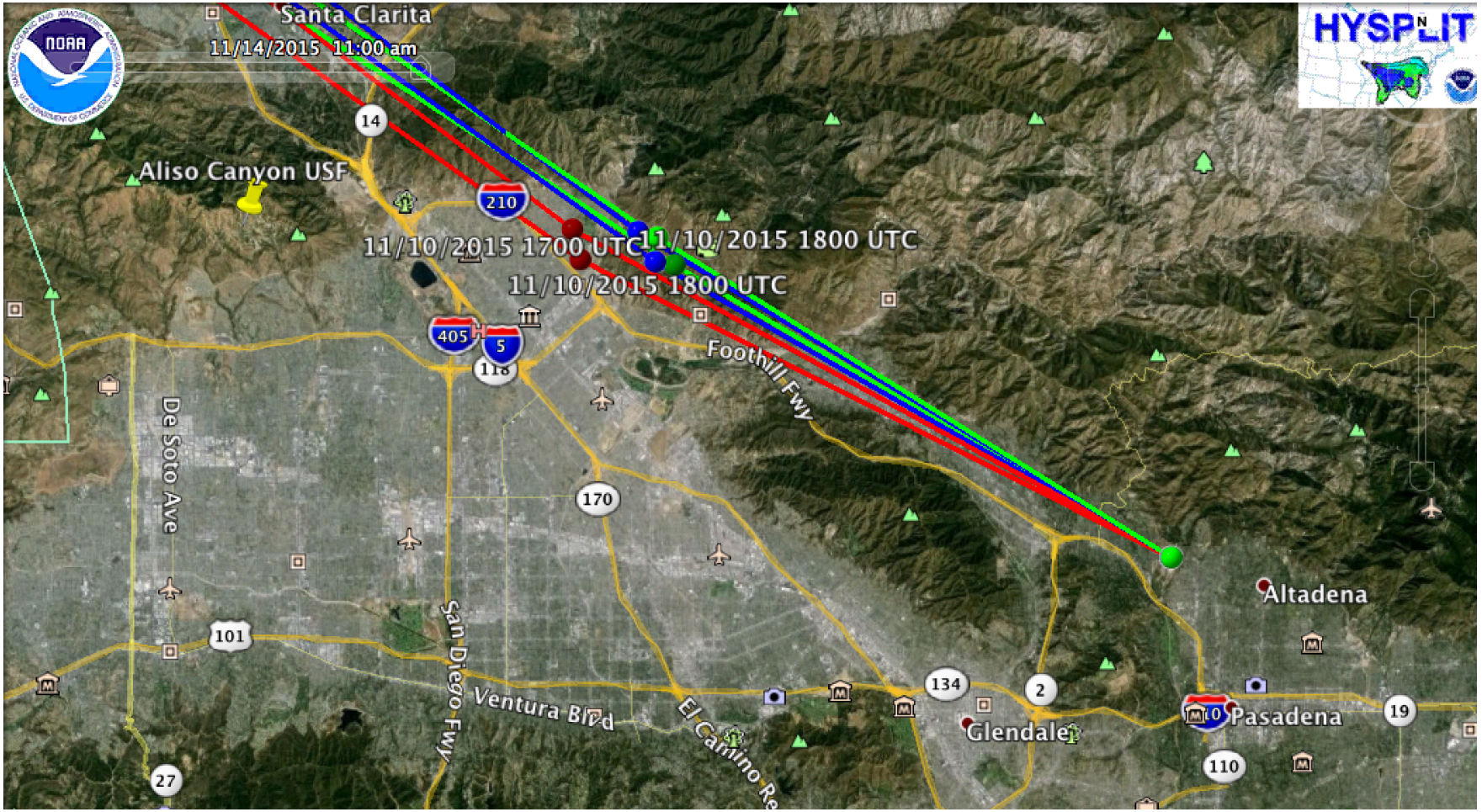




Plots color-coded by $C_2H_6$ (blue=low; red=high). NG leak began on Oct 23 (red arrow)

Only one day with large $C_2H_6$ enhancement: by 1.8 ppb (factor 3) on Nov 10

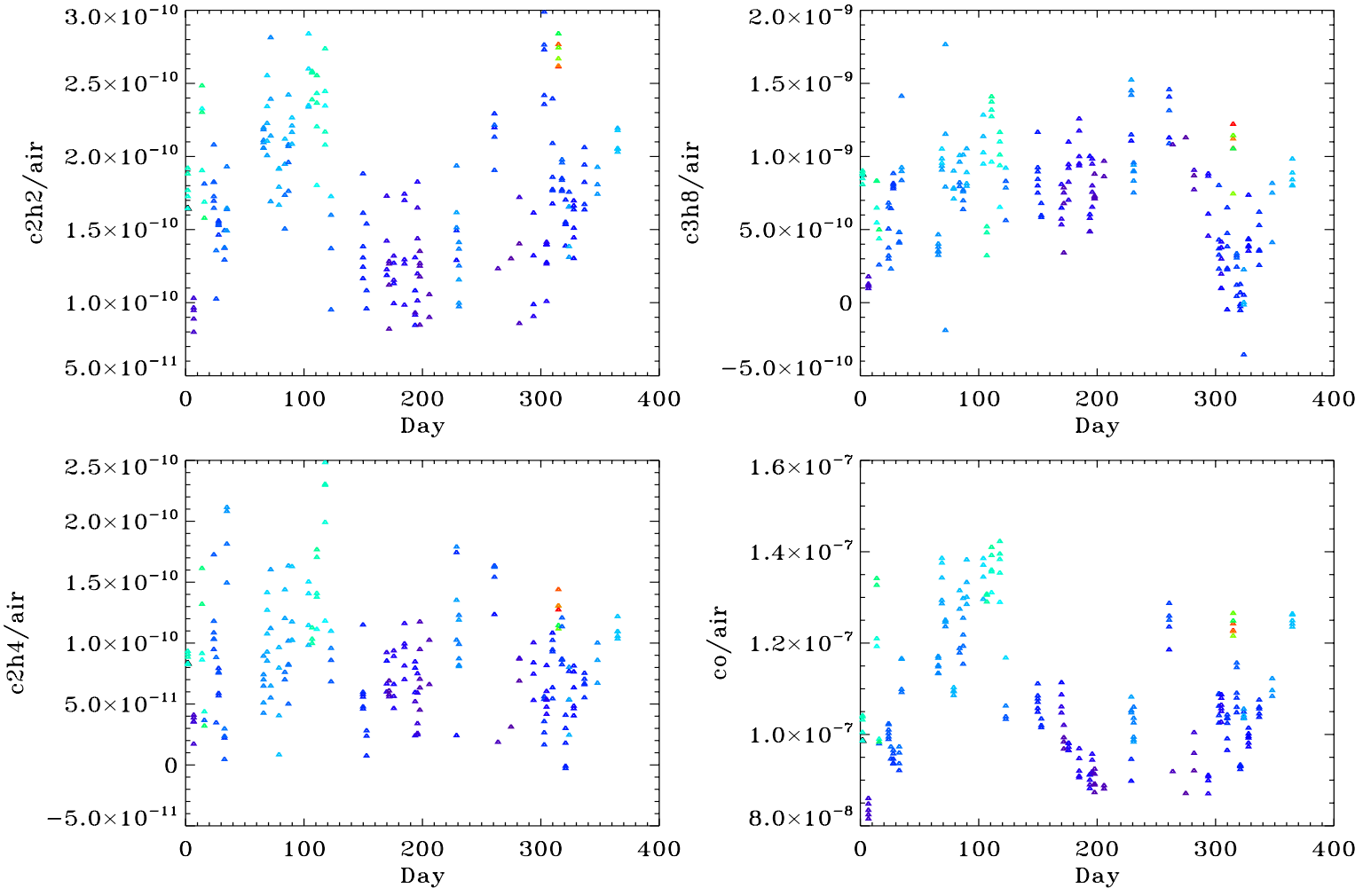
$CH_4$ was also slightly high on this day, but enhancement hard to quantify due to natural variations of 1-2%

# Back-trajectories for Nov 10, 2015



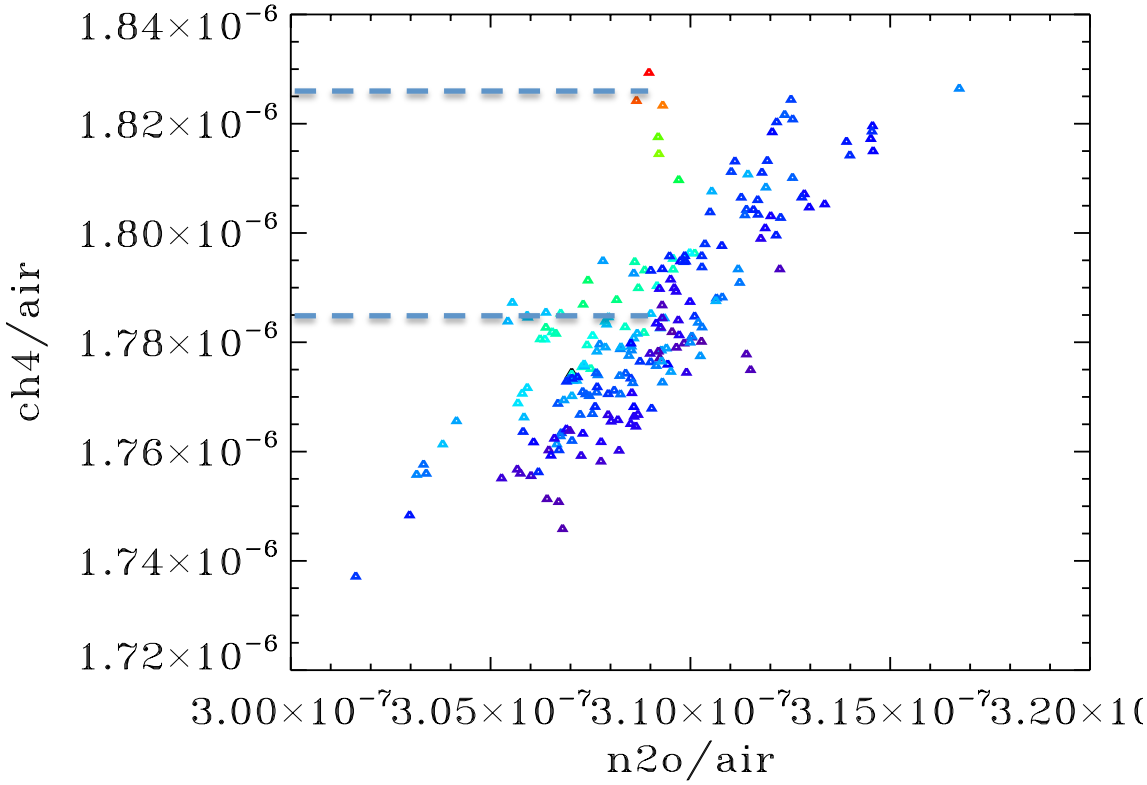

Yellow pin indicates location of Aliso Canyon Underground Storage Facility. Green ball denotes JPL. Within trajectory uncertainties, this represents confirmation that $C_2H_6$ enhancement on Nov 10 was from Aliso Canyon NG leak.

# MkIV 2015 Time Series for other gases




$C_2H_2$, $C_2H_4$, $C_3H_8$ and CO all slightly high on Nov 10, but probably unrelated to NG leak.
Plots color-coded by $C_2H_6$ (blue=low; red=high)

# $CH_4/N_2O$ correlations



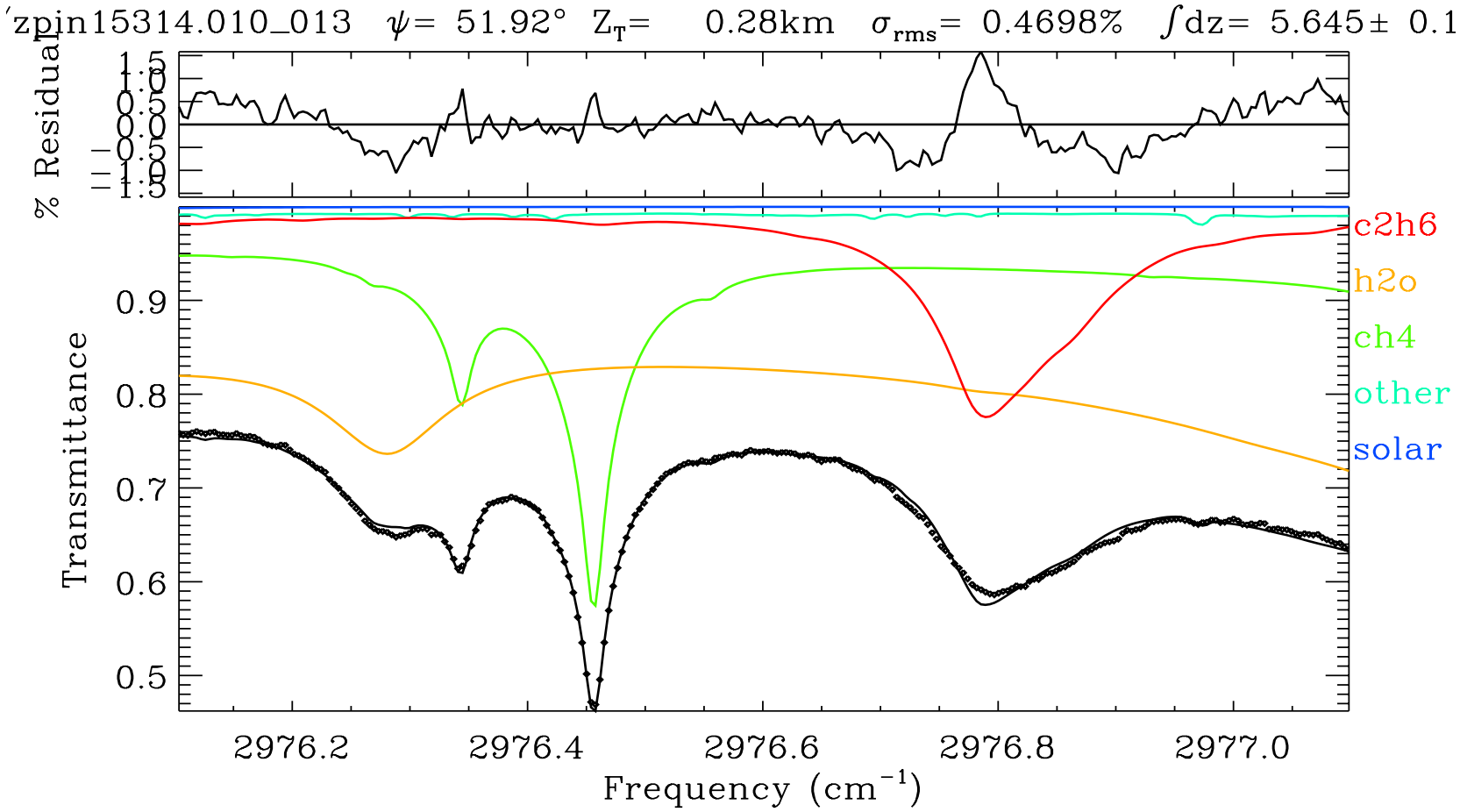

If no $N_2O$ present in leaked NG, then $N_2O$ can be used to account for dynamics.

$CH_4$-$N_2O$ correlation shows 0.04 ppm (2.5%) enhancement in $CH_4$ on Nov 10 (red).

1.8 ppb enhancement of $C_2H_6$. Implies NG is 1.8 ppb / 40 ppb = 4.5% $C_2H_6$

Wikipedia article claims 97,100 tons of $CH_4$ and 7,300 tons of $C_2H_6$, implying leaked NG was 7.0% $C_2H_6$ by weight or 3.7% by mole fraction.

# Spectral fit to $C_2H_6$ Q-branch on Nov 10




$C_2H_6$ absorption (red) is under-broadened due to plume being near the surface, not uniformly mixed throughout lower troposphere.

# NG Leak -- Summary/Conclusions

Factor 3 enhancement of $XC_2H_6$ (1.8 ppb) observed from JPL on Nov 10, 2015.

A 2.5% enhancement of $XCH_4$ (40 ppb) is also seen on this date.

Back-trajectories reveal airmasses passed close to Aliso Canyon, an hour or two before arriving at JPL on Nov 10, 2015.

$C_2H_6$ mole fractions inferred from MkIV columns (4.5%) are not inconsistent with composition of leaked NG (3.7%)

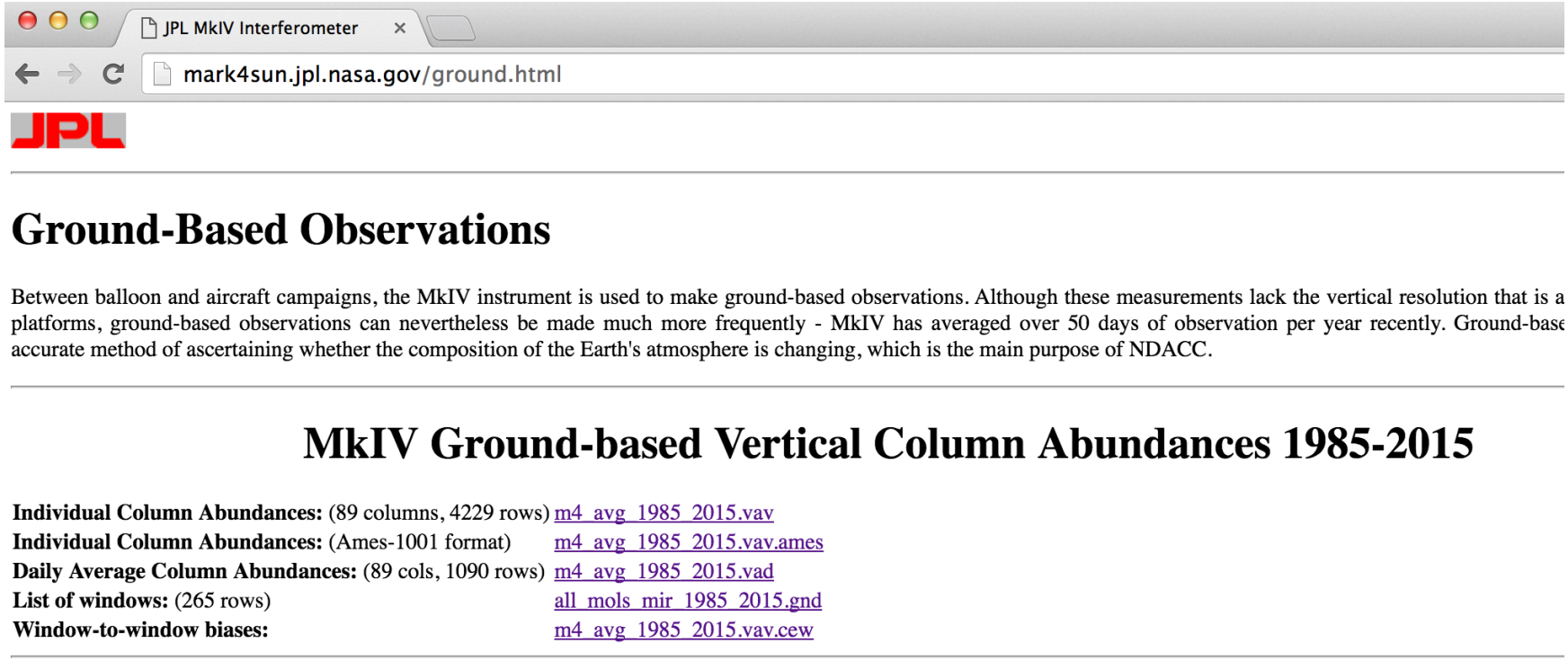
Due to the geography, airmasses arriving at JPL from Aliso Canyon have also traversed the densely populated Northern San Fernando Valley. Small enhancements of $C_3H_8$, $C_2H_4$, $C_2H_2$ and CO are seen on Nov 10, but are within natural variability.

LA is a large source of $C_3H_8$ from LPG. In the US in winter, LPG is approximately 90% propane and 10% butane. NG is only ~1% propane.

# MkIV column data access

The MkIV data shown in previous slides is available from NDACC-IRWG archive and from the website below.

A single file contains 30 years of data for 28 gases from 12 different sites (mainly Barcroft and JPL).



# Herbin et al. [2009]

GEOPHYSICAL RESEARCH LETTERS, VOL. 36, L04801, doi:10.1029/2008GL036338, 2009



## Distributions and seasonal variations of tropospheric ethene ($C_2H_4$) from Atmospheric Chemistry Experiment (ACE-FTS) solar occultation spectra

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Received 14 October 2008; accepted 8 January 2009; published 17 February 2009.

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2003; *Sawada and Totsuka*, 1986]. The dominant mechanism for the removal of $C_2H_4$ from the atmosphere is the fast reaction with the hydroxyl radical OH [*Atkinson et al.*, 1997]. Secondary sinks include reaction with ozone and transport to the stratosphere [*Sawada and Totsuka*, 1986]. Because of this rapid reactivity with OH, ethene has a mean

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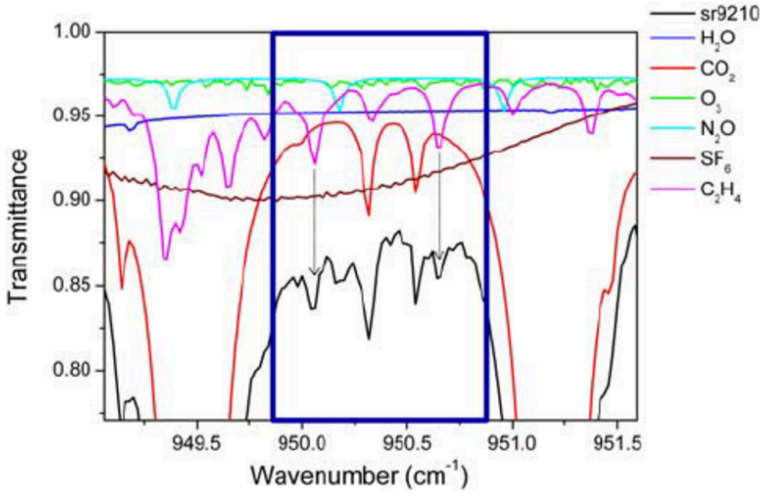


**Figure 1.** Example of ethene spectral signatures in an ACE-FTS spectrum around 9 km tangent altitude, measured at 26.96°N, 101.79°E on April 28, 2005. The black li represents the measured spectrum and the coloured lines t molecule-by-molecule simulations in the spectral windo The dark blue rectangle identifies the spectral micr window used for the retrievals and the dotted arrows t position of the dominant ethene lines in it.

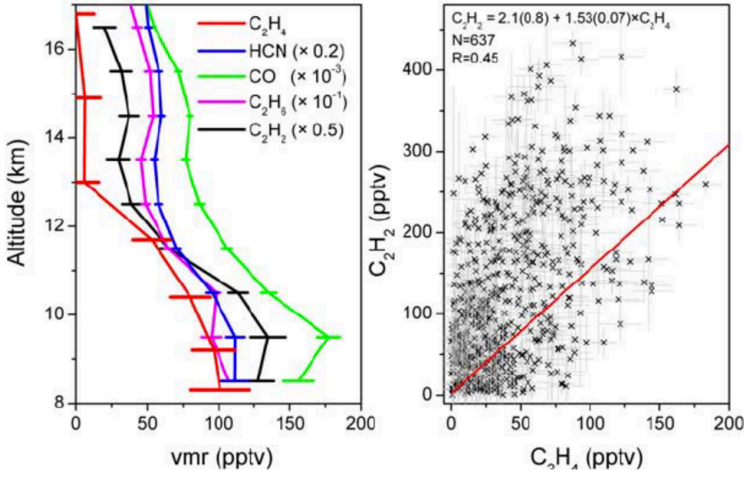


**Figure 4.** (left) Example of retrieved $C_2H_4$ profiles from the same occultation as in Figure 1 and comparison with other carbon tracers. (right) Relationship between the $C_2H_4$ and $C_2H_2$ vmrs around 6 km in the troposphere, considering all measured data points. The red curve is obtained by fitting a line through the data points, weighted by their respective uncertainties. The equation of the linear regression, the number of points (N) and the corresponding correlation coefficient R are given in the upper left corner.

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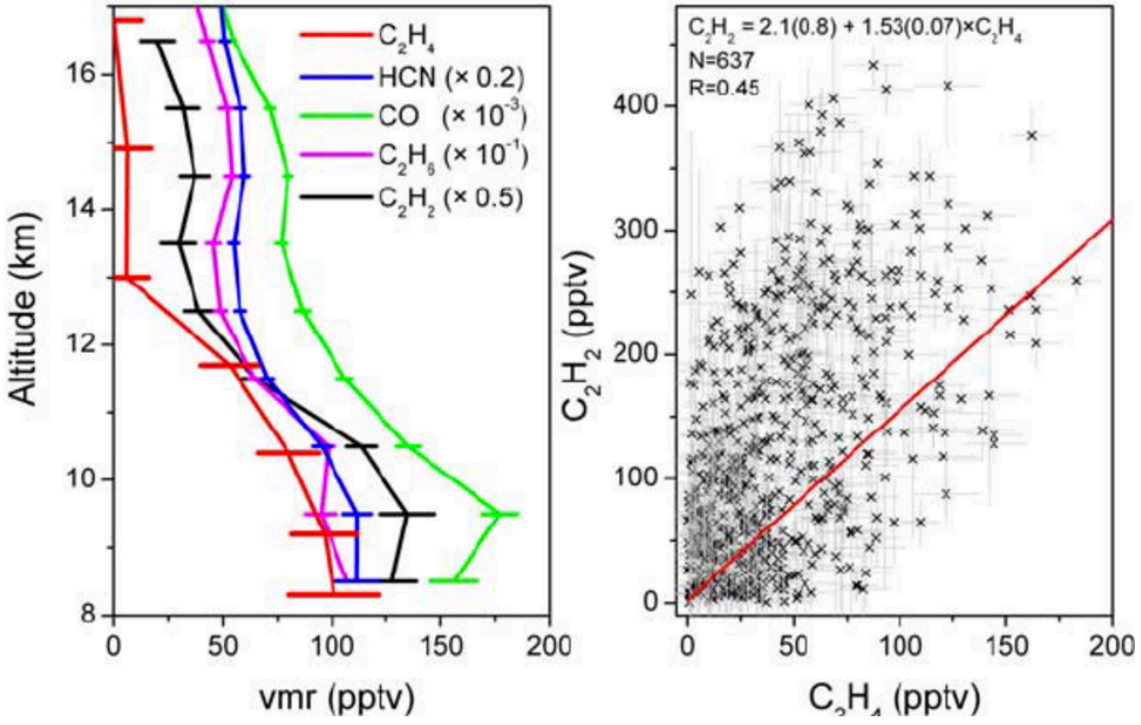


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